



IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of:

ROBERT W. MASON

Serial No.: 09/664,105

Filed: September 19, 2000

For: NON-PHOSGENE ROUTE TO THE MANUFACTURE
OF ORGANIC ISOCYANATES

Attorney Docket No.: LYON 0117 PUS

Group Art Unit: 1625

Examiner: Taylor V.

TECH CENTER 800/2900

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DECLARATION OF ROBERT W. MASON

Commissioner for Patents
United States Patent and Trademark Office
Washington, D.C. 20231

Sir:

I, Robert W. Mason, do hereby declare and state as follows:

1. I am the inventor of the subject matter of U.S. Application Serial No. 09/664,105, filed September 19, 2000.
2. I am employed by Lyondell Chemical Co., where I have been involved in research directed to the manufacture of isocyanates for some 25 years.
3. The vast majority of commercial isocyanates are produced by the phosgenation of amines. Large quantities of toluene diisocyanates ("TDI") methylene diphenylene diisocyanates ("MDI"), and polymethylene polyphenylene polyisocyanates are produced by this method worldwide. Due to the toxicity of phosgene, the industry has long

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sought methods of producing isocyanates without phosgene. However, the majority of the methods proposed have been unsatisfactory due to the low yields produced, the quantity and nature of byproducts produced, and the difficulty of purifying the isocyanate products produced by these methods.

4. I am familiar with the contents of the present application, the Office Actions received with respect to the application, and the prior art cited by the Examiner, i.e. *Okawa*, U.S. Patent No. 5,166,414, *Kober* U.S. Patent No. 3,366,662, and *Faraj* U.S. Patent No. 5,686,645. All three of these patents are illustrative of the search for non-phosgene methods of isocyanate production, *Kober*, for example, having been filed as early as 1964.

5. *Kober* discloses a process for producing an isocyanate by reacting an amine with diphenylcarbonate and pyrolyzing the reaction product. Yields are relatively low, i.e. 50 - 70%, with the remaining 30 - 50% being urea byproducts. Research in our laboratory produced similar results. To my knowledge, the process of *Kober* is not used to manufacture isocyanates due to the low yields and byproducts produced.

6. *Faraj* discloses a process for producing unsymmetrical carbamates and ureas, which he states are useful as isocyanate precursors. Ureas, however, are only useful as isocyanate precursors when reacted with phosgene at high temperature, or for manufacture of volatile isocyanates such as methylisocyanate, by the reaction taught by *Morshel* in U.S. Patent 3,190,905, where the volatile isocyanate can be removed from the reaction mixture before it reacts with the urea starting material or carbamate byproducts to produce biurets and allophanates, respectively. For isocyanates such as TDI and MDI, ureas must be avoided due to the decrease in yield due to these reactions. The carbamates produced by *Faraj* are useful isocyanate precursors, but his yields, from the respective formamide and an alkanol, are low. Examples 7 and 8 report yields of 50% (for a mono-formamide) and 20% (for a bis(formamide)). The low yields, even when using a catalyst, have prevented this process from being acceptable. It should be noted that the process of *Faraj* and that of *Kober* are completely different and employ highly different starting materials.

7. *Okawa* discloses a process for producing aliphatic isocyanates by reaction of an aliphatic formamide with dimethylcarbonate followed by thermolysis of the intermediate product carbamate to the isocyanate. Despite the language appearing at the top of column 5 pertaining to “aromatic amine compounds,” it is clear from the entire *Okawa* patent and in particular the preceding several paragraphs, that *Okawa*’s use of “aromatic amine” does not include compounds where the amine group is linked directly to an aryl ring, but rather to compounds containing an aryl ring to which amine groups are linked through an intervening alkylene group. Examples of the latter are clearly disclosed by *Okawa*, for example N,N’-[1,3-phenylenebis(methylene)]bisformamide (column 4, lines 56, 57), and the formamides of m— and p-xylylene diamine (column 4, lines 66 - 67). These are aliphatic formamides containing an aryl ring. All the Examples employ aliphatic fomamides.

At column 4, lines 63 - 68, *Okawa* indicates that aliphatic amines can be used as starting materials in the “second aspect” of his invention. However, these amines are not reacted with dimethyl carbonate in this second aspect. Rather, they are reacted with methylformate *in situ* in the presence of dimethyl carbonate. As *Okawa* indicates in columns 3 and 4, in the second aspect of the invention, the amine and methyl formate react quantitatively and with a very high reaction rate to form the intermediate formamide, which then reacts with dimethylcarbonate in the presence of alkali catalyst to produce the carbamate. The strongly basic catalyst must then be removed from the carbamate in a separate purification step, following which the carbamate may be pyrolyzed to the isocyanate.

Comparative Examples 3 and 4 of *Okawa* illustrate what happens when conventional transesterification-type catalysts are included in the carbamate during thermolysis: low yields and polymerization.

Okawa teaches only the use of dimethyl carbonate, and for several reasons. First, according to *Okawa*’s “second aspect”, his preferred embodiment, formation of the formamide *in situ* from methyl formate generates methanol, while the subsequent reaction of the formamide with dimethylcarbonate also generates methanol. Thus, only one byproduct alcohol is generated, whereas if a different dialkyl carbonate such as diethyl or dipropyl

carbonate had been used, the byproduct mixed alcohol stream would have to be distillatively separated to provide methanol and the second alcohol as saleable byproducts or recyclable byproducts.

Second, and most importantly, dimethyl carbonate was selected by *Kober* so that dicarbamates of arylaliphatics such as xylylene bisformamide and aliphatics such as N,N'-[1,3-cyclohexylbis(methylene)] bisformamide can be thermolyzed in high boiling solvent to produce a vapor phase containing very little solvent, but containing methanol and the desired isocyanate product. The methanol and isocyanate can be rapidly removed at lower than atmospheric pressure (1 - 500 mmHg) and easily separated due to their very different boiling points. Had a dialkyl carbonate such as diethyl carbonate or dipropyl carbonate been used, not only would the vapor phase be expected to contain a greater amount of high boiling solvent, but moreover, the vapor phase would necessarily be at a higher temperature due to the higher boiling points of the respective alkanols, thus leading to greater potential for isocyanate polymerization. Finally, the separation of the alkanol from the isocyanate would have been more difficult due to their boiling points being closer.

8. As one skilled in the art, reading *Okawa*, I would be motivated to produce aliphatic isocyanates by his method, but employing dimethyl carbonate only. I would not be motivated by *Okawa* to produce isocyanates other than aliphatic isocyanates such as hexylene diisocyanate, xylylene diisocyanate, or hydrogenated xylylene diisocyanate, because in my opinion as one skilled in the art, *Okawa's* process is limited to these kinds of isocyanates. I also would not be motivated to employ carbonates other than dimethyl carbonate, as *Okawa* discloses several reasons for using dimethyl carbonate which do not apply to other dialkyl carbonates. Moreover, it is highly suggestive that despite the fact that numerous diorgano carbonates were known at the time of *Okawa*, he did not mention or even hint at using any other diorganocarbonate.

9. The Examiner has premised his rejection on the combination of three references, *Okawa*, *Kober*, and *Faraj*. It is my understanding that in order to base a rejection

on a combination of references, there must be some motivation for one skilled in the art to combine these references. I find no such motivation.

All three references have only one common link: the desire to provide a non-phosgene method of isocyanate production. However, there the similarity ends. *Okawa* produces aliphatic isocyanates by reaction of a formamide, preferably prepared *in situ* from an amine and dimethylcarbonate, with dimethylcarbonate, a very specific dialkylcarbonate. *Kober* employs a very different reaction, the reaction of an amine with a diarylcarbonate, preferably diphenyl carbonate. These reactions employ different starting materials, and have completely different reaction mechanisms.

Faraj is a further, unrelated reaction, which employs a formamide and an alcohol. No carbonate of any kind is used. While in the *Faraj* reaction the alcohol is a reactant, in *Okawa*, it is a byproduct. While *Okawa* requires dimethyl carbamate so that a low boiling alcohol product is obtained, *Kober* employs a diaryl carbonate, the "alcohol" byproduct of which is a phenol, having a much, much higher boiling point than methanol.¹

As one skilled in the art, I would not be motivated to combine any of these references for any purpose, as all three are fundamentally different. In particular, I would not be motivated to combine *Okawa* with *Kober*, as first, there is no suggestion in either reference which would motivate one skilled in the art to combine these references, and second, as one skilled in the art, I find that *Okawa* teaches against the proposed combination.

10. Several laboratory experiments were made with the process of *Okawa* to test the feasibility of employing dimethyl carbonate to produce aryl isocyanates, i.e. isocyanates in which the isocyanate group is attached directly to the aryl ring as in TDI, and not an aryl group-containing aliphatic isocyanate such as xylylene diisocyanate as taught by *Okawa*.

¹ methanol, b.p. 64.5°C; phenol, b.p. 182°C.

A series of reactions were run at various temperatures and both uncatalyzed and catalyzed with a variety of catalysts, including *Okawa's* preferred catalyst, sodium methylate. The formamide used was the bis(formamide) of 2,4-toluene diamine, as used in Examples 2, 3, and 4 of the subject invention specification. Dimethyl carbonate, the reactant employed by *Okawa* was used. The results are tabulated in the Table below.

Reaction Temp.	Catalyst	Result
150°C	None	No reaction
90°C	DMAP	N-methylated amines and formamides
150°C	DMAP	N-methylated amines and formamides
150°C	DMAP, methanol	Mostly N-methyl amines
150°C	NaOCH ₃	70 % di-N-methyl-formamide
90°C	NaOCH ₃	10 % N-methyl-formamide in 22hr
90°C	NaOCH ₃ , phenol	Amines and ureas (hydrolysis)
90°C	Et ₃ N, phenol	6 % urea in 20 hr.
170°C	DMAP	di-, tri- and tetra-N-methylated products

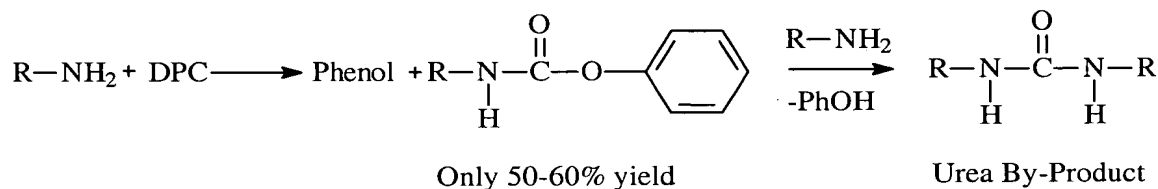
(DMAP = 4-(N,N-dimethyl-amino)-pyridine)

None of the desired intermediate carbamate isocyanate precursor was obtained. Instead, formamide hydrolysis to free amines and ureas and N-methylation of the amines and formamides was observed. These results are consistent with those for the reaction of aniline with dimethyl carbonate reported by Gurgiolo in U.S. Patent 4,268,684. Thus, for the claims directed to preparation of aryl isocyanates, in view of Gurgiolo, one skilled in the art would further not be motivated to employ the process of *Okawa*.

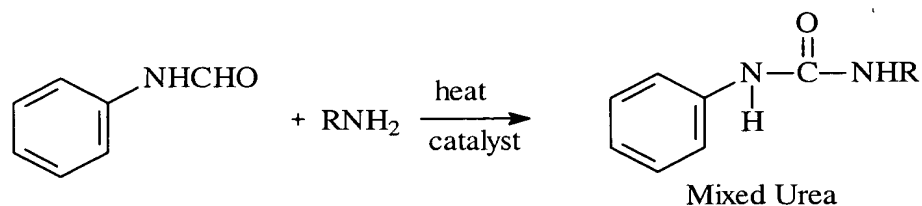
11. For all the reasons expressed above, the claimed invention has produced new and unexpected results. The high isocyanate yields are particularly surprising. None of the cited references, *Kober*, *Okawa* or *Faraj*, are suitable methods for the production of aromatic isocyanates. Because the amine group is not "protected" in *Kober*, the desired phenyl carbamate product is free to react with additional amine and generate undesirable ureas. The

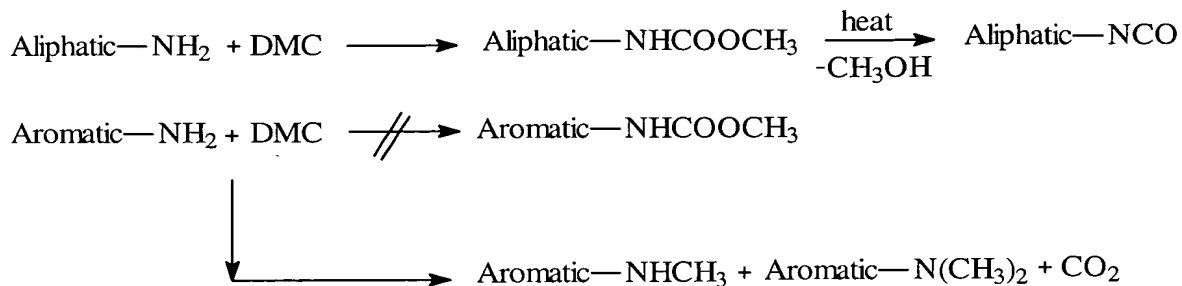
claim that such ureas are suitable intermediates for the eventual formation of isocyanates, as in *Faraj*, is simply not true. No matter how they are made, by DPC reaction with free amines or by the thermolysis of formamides in the presence of free amines, ureas cannot be readily converted to isocyanates except by high temperature reaction with phosgene. Despite the generality of claim 1 of *Okawa*, that formamides can be converted to urethanes with dimethyl carbonate, aromatic formamides are not converted to urethanes with dimethyl carbonate, but instead produce N-methylated products, just as Gugliolo demonstrated in the reaction of dimethyl carbonate with free amines. It is not obvious to me, someone skilled in the art of isocyanates for over 25 years, that combining the low yield aromatic isocyanate processes of *Kober*, *Okawa*, and *Faraj* would intuitively produce the results I demonstrate in my application.

Kober:



Faraj:



Okawa and Gurgiolo:

12. I also note that the Examiner has rejected the claims as indefinite, and as non-enabled. To one skilled in the art, the specification is clearly enabling. Selection of reactants such as the amine from which the formamide is to be produced, the formamide itself, catalysts, reaction temperatures, etc. can all be made by one skilled in the art without undue experimentation. For example, the temperature at which the carbamate intermediate decomposes can be readily ascertained by use of common and readily available techniques, or can be monitored by gradually increasing the reactor temperature and monitoring isocyanate production by HPLC, GC, etc. To one skilled in the art, the specification is enabling and the claims definite.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code.

Dated: 2/21/03

Robert W. Mason
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